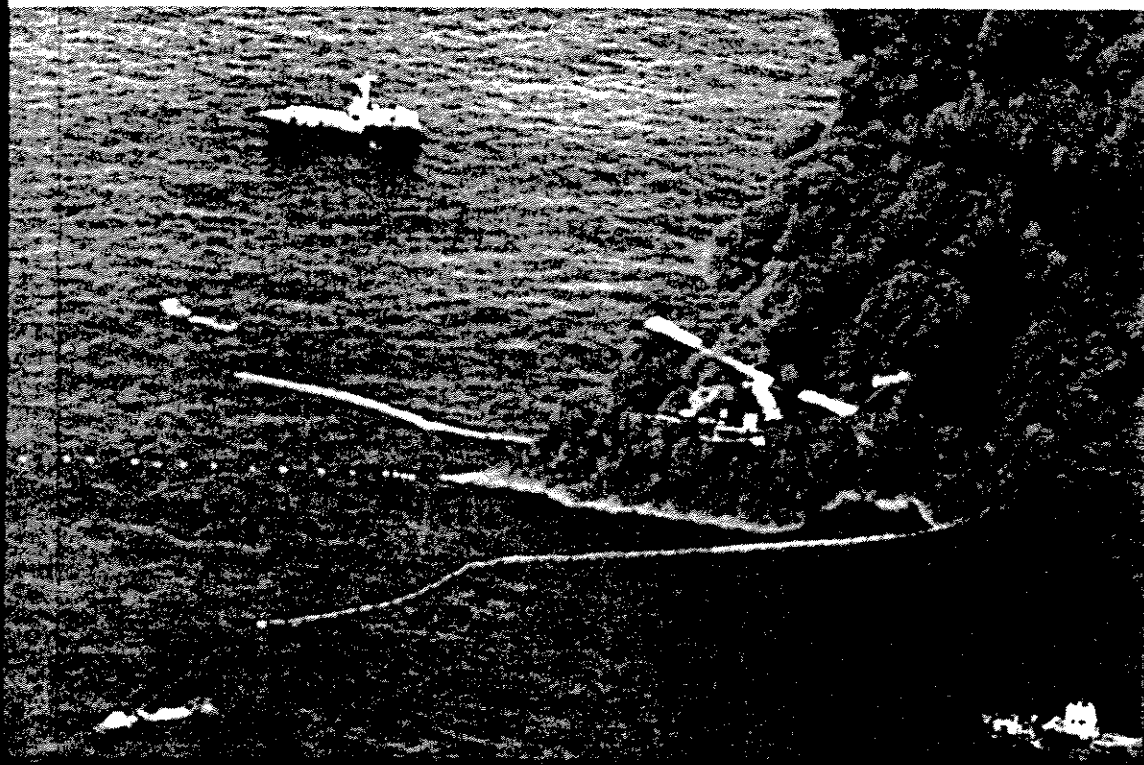


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TESTING OF OIL SPILL DISPERSANT EFFECTIVENESS IN THE LABORATORY

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Introduction

Many different types of dispersant test procedures and apparatuses¹ are described in the literature. One estimate places this at 50 different tests or procedures. Of these, only a handful are in common use. These include the Labofina or rotating flask test, the French dilution test, the Mackay or MNS (Mackay-Nadeau-Steelman) test, the swirling flask test, and the SET (Simulated Environmental Test Tank).

Several investigators have reported results of apparatus comparison tests.¹⁻¹² All these have concluded that the results of the different tests do not correlate well, but some conclude that some rankings are preserved in different tests. Generally, the more different types of oil tested, the fewer results correlate. This paper reviews Environment Canada's studies of laboratory tests and shows that laboratory tests can be designed to give a reasonable value of oil dispersion given that the parameters of turbulent energy, oil-to-water ratio, and settling time are set at optimal values.

The most common laboratory apparatuses are listed in Table 1. In some cases different protocols have been described in the literature for the same apparatus. There is no reason why different protocols cannot be used on the same apparatus.

Previous comparisons of the different apparatus have been limited. Byford and Green compared the Labofina and Mackay tests on a series of 2 oils and 5 dispersant combinations.² They concluded that the ranking of effectiveness between the two tests correlated well, although the numerical values had significant variation. Meeks compared EPA, Russian, Warren Springs, and French dispersant effectiveness results for two oils and three dispersants.⁵ He concluded that the results of the tests are sufficiently different that even the rank of effectiveness is not preserved. Daling and Nes compared the Mackay and Labofina Apparatus using 2 oils and 7 dispersants.³ They concluded that numerical correlation among results is poor, but that the rank of effectiveness is consistent between the results generated using the two apparatuses. Daling compared the Mackay, Labofina and IFP devices for three different oils, with three different water contents and one dispersant.¹² This comparison showed that the numerical results were not correlatable, and the ranking of effectiveness also varied significantly. The present author and co-workers compared the Labofina, Mackay, oscillating hoop and swirling flask apparatus for 10 oils and three dispersants.¹ We concluded that the correlation

Testing of Oil Spill Dispersant Effectiveness", In Proceedings of the Arctic Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, Ontario, pp 905-941, 1994.

¹ note: the most generally-accepted plural of apparatus is apparatuses. This will be used in this paper to distinguish a single apparatus from several

TABLE 1

SUMMARY OF LABORATORY TEST APPARATUS

	TEST NAME	ALTERNATE NAME (S)	ENERGY SOURCE	WATER VOLUME (L)	PRIME USE
⇒	LABOFINA	WARREN SPRINGS ROTATING FLASK	VESSEL ROTATION	0.25	REGULATORY GENERAL
⇒	MACKAY	MNS MACKAY-NADEU-STEELMAN	AIR STREAM	6	REGULATORY GENERAL
⇒	SWIRLING FLASK		VESSEL MOVEMENT	0.12	REGULATORY GENERAL
⇒	SET	SIMULATED ENVIRONMENTAL TEST TANK	CIRCULATING PUMP	119	REGULATORY
⇒	IFP	DILUTION TEST FRENCH STANDARD	OSCILLATING HOOP	16	REGULATORY GENERAL
⇒	CASCADING WEIR	MACKAY FLUME	FALL OVER WEIR	CONSTANT FLOW 0.5 L/s	EXPERIMENTAL
⇒	FLOWING COLUMN		FALL DOWN TUBE	1 (FLOWING)	EXPERIMENTAL
⇒	CONCENTRIC TUBE	BOBRA	WATER FLOW	CONSTANT FLOW (~0.05 L/s)	EXPERIMENTAL
⇒	OSCILLATING HOOP		OSCILLATING HOOP	35	EXPERIMENTAL
⇒	WAVE-PLATE TANK	SOUTH AFRICAN BP SUNBURY	MOVING PLATES	30	REGULATORY GENERAL
⇒	EXDET		WRIST-ACTION SHAKER	0.25	EXPERIMENTAL
⇒	HIGH-ENERGY		MOVING VESSEL	5	EXPERIMENTAL
⇒	SPINNING DROP	INTERFACIAL	WATER MOVEMENT	<0.05	EXPERIMENTAL
⇒	BLENDER		PROPELLER	1.5	EXPERIMENTAL

among the numerical results was poor and that rank of effectiveness correlated only weakly. The oscillating hoop test results, in particular, correlated poorly with other results. Clayton and Payne compared several tests and concluded that they do not yield similar results except for some of the lower energy devices.¹¹ The ranking of dispersant effectiveness is generally preserved throughout most tests.

Some work has been done on finding the reason for the poor correlation between test results. All of the above investigators cite energy as being the most significant factor. The general conclusion has been that the differences in energy levels and the way these have been applied to the oil/water mixture result in effectiveness values that are unique. The investigators followed the specified test procedure when using an apparatus and did not vary any of the conditions. The only exception to this was the study by Daling and Ness, in which the dynamic sampling normally specified for the Labofina and Mackay apparatus was varied up to 10 minutes.³ This factor was found to be very important in improving correlation between the effectiveness values yielded by the two apparatuses. The present authors have published several studies on the comparison of laboratory tests and have found specific reasons for the lack of correlation.¹³

Laboratory Tests and The Issues

The most important issue regarding laboratory tests is the purpose of the test. Much time has been lost discussing tests when, in fact, the primary issue is the purpose. If the purpose of the test is, for example, to screen ineffective products from effective products, and the results correlate well with other tests or other set standards, then the test is satisfactory for that purpose. If the test is designed to study physical relationships, then there should be measurable correspondence to the sea or at least to other identifiable physical phenomena. Tests for physical studies may require access to the oil-water interface, whereas other tests may not. One of the problems of the current state-of-the art with laboratory testing is that many workers attempt to use one test for many purposes, often running into problems of design limitations.

The second issue of laboratory testing is the correspondence to reality. While it is acknowledged that energy levels and similar parameters should have some correspondence to the real world, it is recognized that not all parameters can be so easy. There exists no means to measure energy for example. Proponents of "at sea" testing state that no laboratory testing should be done - implying that these are all unreal. It is suggested that basic physical principles are operative both in the laboratory and at sea. At-sea testing has also severe limitations. Measurements are very noisy, some measurements cannot be done at all. At sea studies are costly and inevitably very few experiments can be done. Ability to spill oil for research purposes at sea is very limited and is becoming increasingly difficult in most countries. Measurement of data at real spills is very fraught with difficulties. Measurement techniques for open situations are at best crude and in most cases are entirely absent. Most current at sea measurements are visual observations combined with secondary measurement (such as fluorescence) at one point under the water. The laboratory situation has many benefits in terms of being able to measure and control parameters. Ideally, both types of experimentation should be performed.

The next issue on laboratory testing is standardization. Historically, the techniques by which an actual test was used, were generally not described in detail. Some procedures are crucial to the outcome of the test, but have not been studied and optimized. There has been a strong tendency in the past to develop a "national" test and

then try to persuade other countries to adopt the test. Most of these tests have not been studied in depth and their procedures were not optimized.

Another concern has been the use of "homemade" apparatus. Most of the currently-popular tests except for the swirling flask use homemade agitators or shakers. This leads to the lack of compatibility and often to an inability to correlate data between laboratories. The present authors worked on the MNS test, as an example of a homemade test.¹ Two apparatuses in the same laboratory could not yield the same result. Differences were many, but primarily related to the prime mover for the air. It was found that a vacuum cleaner motor was used in the original apparatus. That particular model of vacuum cleaner was no longer available and other vacuum cleaners either were too vigorous or too weak. This occurred despite three techniques for measuring the energy input. Our laboratory has seen several examples of this problem. One European test cannot be re-created in North America because of the power differences. Even the use of a converting transformer with a European apparatus did not yield comparable results. Development of a new dispersant test should first be done based on an existing, common and standard laboratory prime mover.

A major concern in laboratory testing is the reliability of measuring techniques. Historically, these techniques have not been questioned and assumed reliable. Techniques for measuring the oil in the water are not entirely reliable. Techniques for measuring energy are nonexistent. Much more work and thought must be put into the measurement of necessary parameters before advocating a particular test.

A newly-developed test should be subjected to analysis in which every relevant parameter is varied. This includes rotation speed, temperature, oil-to-water ratio, types of oil and dispersant, etc. This is essential to ensure that the test is not operating at some critical point. Examination of many existing tests has shown problems and anomalies.

The final "philosophical" issue on laboratory testing is the matter of standardization for an entire test along with procedures. While this is ultimately desirable, the current need for this is questionable. Most testing is now done for the screening of products for national compliance. While some universality is desirable, its benefits may not be measurable. Standardization will involve costs. Standard oils and dispersants will be necessary to check equipment and procedures. Staff will require more training and practice. Most laboratories do not have dedicated staff performing tests. This would cause extra complications.

Wall Effect

A very major concern in laboratory testing is the effect of the walls of the apparatus. Ideally, there should be no contact of the oil with the walls. Sometimes, contact with the walls becomes unavoidable. An example of the latter is the Environment Canada high energy test, where the wall is used to generate high levels of turbulence. A series of tests was conducted to assess the wall effect of several apparatuses.

Apparatuses were operated according to standard procedures except as noted in this paper. The apparatus was operated with light Bunker C oil and no dispersant. After the specified mixing time was complete, the remaining surface oil was collected with sorbent (3M brand). The water from the apparatus was drained. The oil clinging to the sides was then extracted by rinsing the apparatus with dichloromethane which was subsequently analyzed for oil using the colorimetric method noted in the appendix. The Labofina test employs a 250-mL separatory funnel which is rotated at 33 rpm.¹⁴ The swirling flask test, developed by Environment Canada, employs a 120 mL beaker and

a standard laboratory shaker. Standard procedures for operating this device appear in the appendix to this paper. The high energy test was developed at Environment Canada to study the relationship of dispersant effectiveness and energy. Procedures to operate this device are in the literature.¹⁵ The MNS test employs an air stream to energize water.¹⁷ The results for the loss measurement are given in Table 2. Of the four apparatuses tested, only the swirling flask shows a low rate - this being less than 2% of the starting oil volume. The MNS shows loss rates from 13 to 19%. The Labofina or Warren Springs test shows loss rates of 3 to 54% and the high energy test, 19-54%. The loss rates are in line with expectations. The swirling flask has a circular motion that causes a vortex allowing little contact with the oil. The Labofina moves the oil-water interface completely around the vessel - resulting in a very high loss rate. The high energy test makes use of the walls to generate high turbulence and thus has high contact with the walls. The variation of loss to walls with shaking time is illustrated in Figure 1. As expected, loss increases with shaking time in all apparatus. The effect of increasing the oil-to-water ratio to very small quantities of oil also increases the percentage loss, as expected. This is illustrated in Figure 2 where this effect is shown with the high energy device.

EFFECT OF OIL-TO-WATER RATIO AND SETTLING TIME

This section focuses on two of the variables important to laboratory dispersant tests, the oil-to-water ratio and the settling time, that time between the taking of the sample for analysis and the time that the energy is no longer applied to the apparatus. Increased settling time allows large, unstable oil droplets to rise to the surface before the sample is taken and thus reduces the effectiveness values to represent only the more stable dispersions. The oil-to-water ratio varies dramatically in the various test protocol.

Experimental

Apparatuses were operated according to standard procedures except as noted in this paper. The oil-to-water ratio was changed by varying the amount of oil added to the system and the water amount was kept constant at the normal specified level. The settling time was varied by sampling water from the apparatus after the specified time. In the flowing cylinder, analysis of dispersion is performed by trapping oil in a filter and analyzing oil in this filter. Settling time cannot be varied in this apparatus.

The oscillating hoop apparatus employs a hoop which is moved up and down at the surface of 35 litres of water. Detailed protocols for operating this apparatus have been described previously.¹⁶ The swirling flask apparatus uses a 125-mL Erlenmeyer flask with a standard laboratory shaker to induce a swirling motion to the contents. Procedures for this device are also detailed in the appendix. The Mackay apparatus uses a high-velocity stream of air to energize 6 L of water. Both operating procedures and construction details are documented.¹⁷ The Labofina test employs a 250-ml separatory funnel which is rotated at 33 rpm.¹⁴ Analysis for all four apparatuses is performed by taking a sample of water from the test vessel after the run is complete, extracting the water with a solvent and measuring the absorbance at three visible wavelengths, and then assigning effectiveness based on a calibration curve. All runs were performed with dispersant already mixed in the oil at a ratio of 1 to 25 by volume. This practice was adopted to achieve more repeatable results as determined in earlier experiments where both premixed and drop-wise additions were used.¹ Physical properties of the oils used in these tests are given in Table 3. The dispersants used

Table 2

Measurement of Loss to Vessel Walls**High Energy Test**

Oil-to-Water Ratio	Energy (rpm)	Loss (%)	Std. Dev.
1:40000	400	39	4
	300	43	4
	200	41	3
	100	42	3
1:20000 (standard)	400	26	4
	300	19	1
	200	26	2
	100	31	2
1:10000	400	50	5
	300	25	3
	200	25	2
	100	28	2
1:5000	400	50	3
	300	46	9
	200	32	2
	100	54	2

Tests with Time as Variable - energy = 400 rpm

oil-to-water ratio = 1:20,000

Time (min)	Loss (%)	Std. Dev.
60	46	7
40	41	3
20	32	0
10	30	2

Swirling Flask

Oil-to-water ratio	Time (min)	Loss (%)	Std. Dev.
1:1200 (standard)	60	1	0.5
	40	0.5	0.3
	20	2	0.7
1:600	60	0.8	0
	40	2.1	0.1
	20	1	0
1:300	60	0.8	0.4
	40	0.8	0.6
	20	0.4	0.3

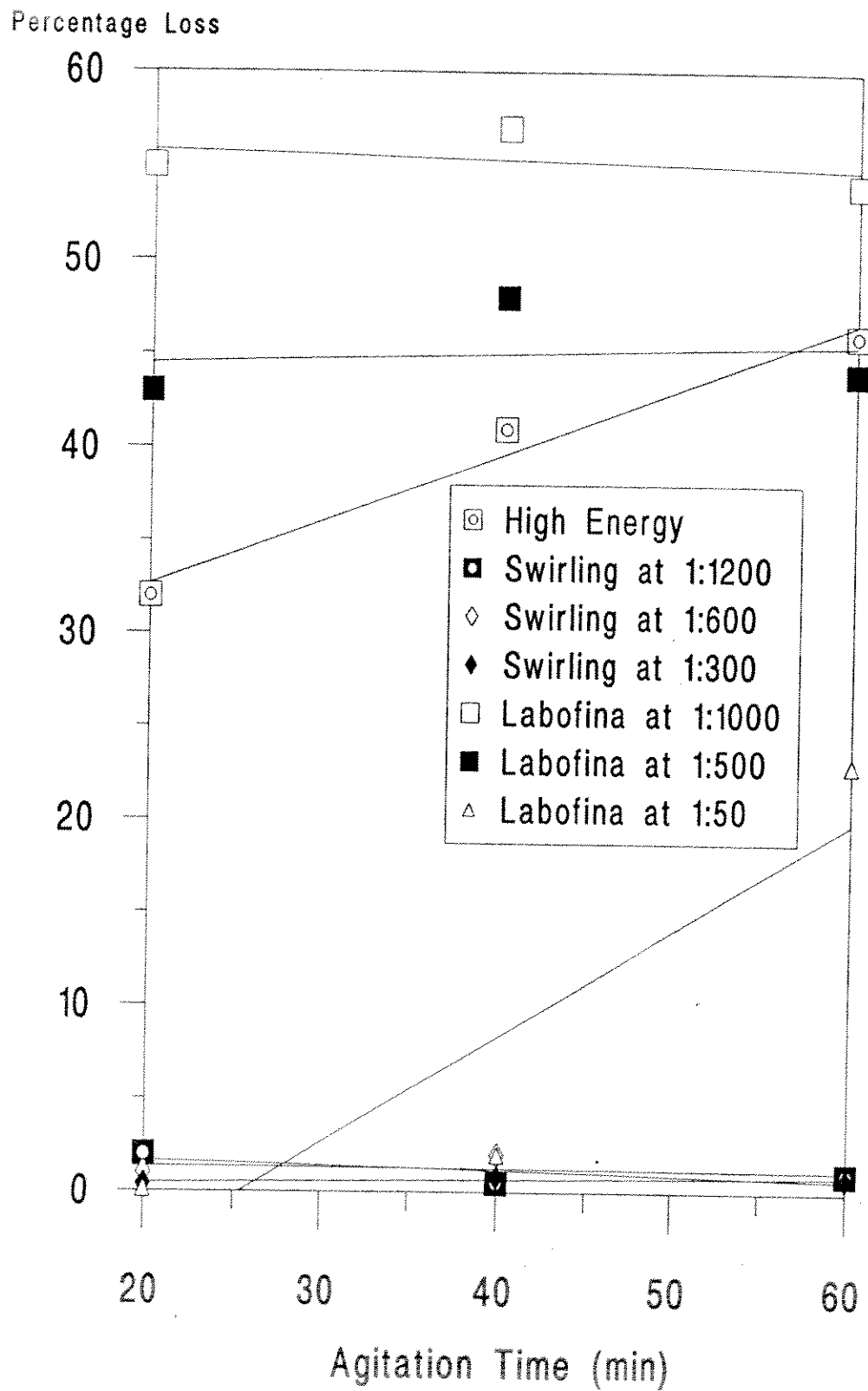
Labofina

Oil-to-water ratio	Time (min)	Loss (%)	Std. Dev.
1:1000	60	54	11
	40	57	2
	20	55	4
1:500	60	44	16
	40	48	5
	20	43	2
1:250	60	31	20
	40	18	5
	20	14	1
1:50 (standard)	60	27	23
	40	3	2
	20	3	0.1

MNS

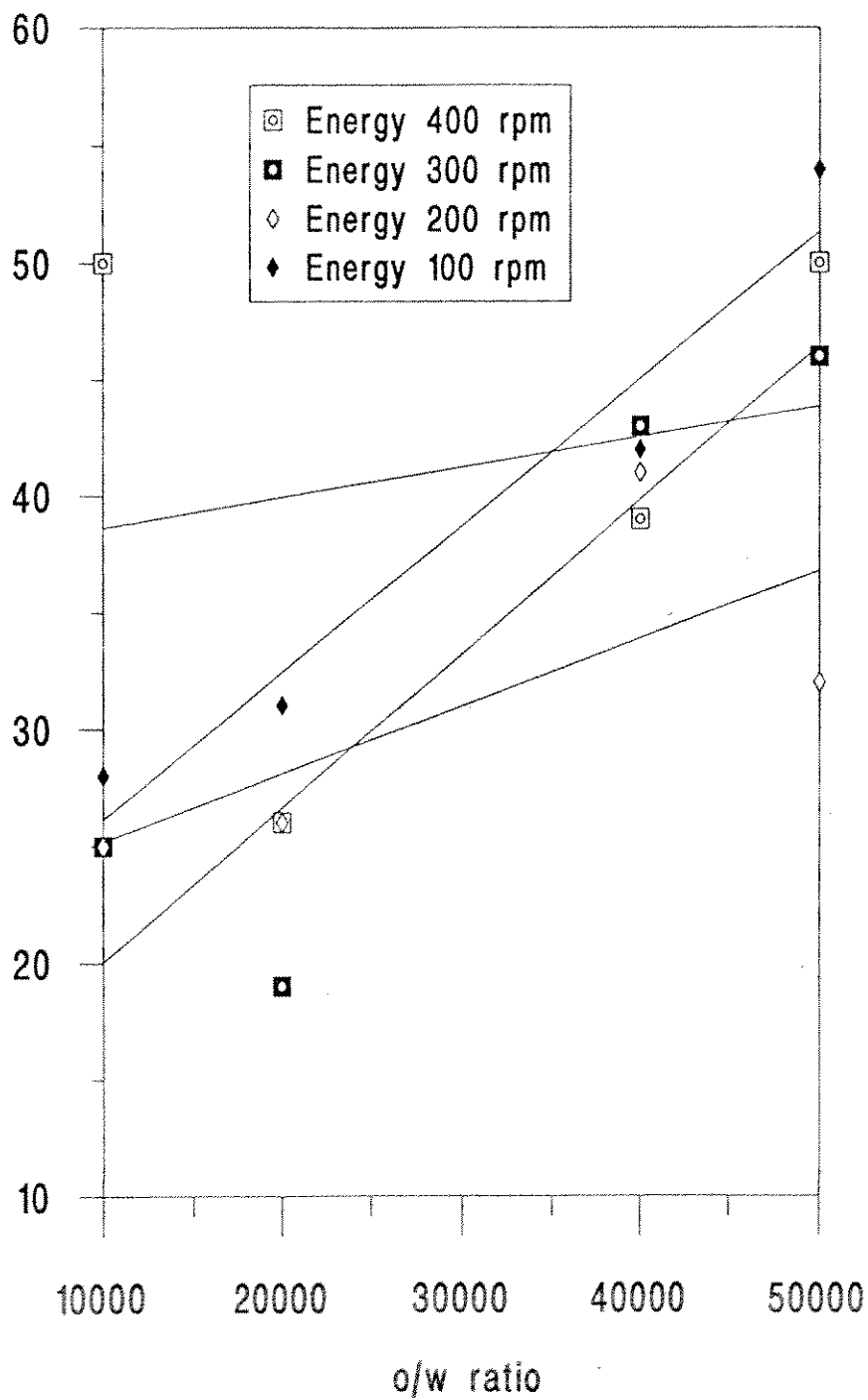
Oil-to-water ratio	Time (min)	Loss (%)	Std. Dev.
1:600	30	13	1
1:1200	30	19	2
1:2400	30	17	1

Figure 1 Loss to Vessel Wall with Time



**Figure 2 Losses in The High Energy Device
Variation With Energy and Ratio**

Percentage Loss



include the Exxon products Corexit 9527 (abbreviated C9527 in some tables in this paper) and Corexit CRX-8 (abbreviated CRX-8), and the British Petroleum product, Enersperse 700 (abbreviated EN 700). In two tests, experimental dispersants were used and were designated "test product" and "experimental dispersant".

The flowing cylinder test was developed at Environment Canada's laboratory. The basic operating principle is that water is continuously removed from the bottom of a cylinder and replaced at the top of the cylinder.¹³ This circulation draws dispersed oil into the water column and ultimately into a filter which removes the oil and the clean water returns to the top of the cylinder where it drops down the cylinder wall providing energy for dispersion. The length of the cylinder is sufficiently long that only small (1 to 30 micron diameter) particles enter the hose.

For every value presented here, at least two independent experiments were run. If values did not agree within the normal repeatability values for a particular device, repeat runs were performed until at least three values were within the repeatability percentage. The repeatability of results for each device was taken as the mean difference between duplicate runs before performing repeat runs. It can also represent the standard error or the plus and minus value noted behind many measurements. The standard error for each device is as follows: swirling flask - 3%, flowing cylinder - 5%, Mackay - 9%, Labofina - 7%, and oscillating hoop - 9%. Maximum errors can be as much as 40% for the Mackay and Labofina tests and as much as 20% for the other tests.

The Role of Oil-To-Water Ratio and Settling Time

The effects of oil-to-water ratio were first evaluated by changing the ratios in experiments using the oscillating hoop and swirling flask apparatus. These results are shown in Figure 3. The effect of changing the oil-to-water ratio in the oscillating hoop is surprisingly large and results in a sharp peak at an oil-to-water ratio of 1:500. The overall effect is the same for two apparatuses and for the different oil-dispersant combinations. The effectiveness drops down at ratios below 1:200 and dramatically so at ratios as low as 1:20. The maximum effectiveness is seen at ratios around 1:500 and from 1:1000 becomes relatively stable up to 1:3000. It is suggested that this variation is the result of different mechanisms of dispersant action. At low oil-to-water ratios, there is a large amount of surfactant present and this surfactant interacts forming micelles rather than interacting with the oil. At low ratios, there are sufficient numbers of micelles to solubilize portions of the oil. At high oil-to-water ratios the primary interaction between oil and surfactant is the formation of dispersed particles. At ratios close to 1:500, both mechanisms come into play and apparent dispersion is increased.

The flowing cylinder was used to test the effect of increasing the oil-to-water ratio from 1:4000 up to 1:120,000. This was achieved by placing incrementally smaller amounts of oil and dispersant mixture into the apparatus. The oil-to-water ratio noted here does not take into account the recirculated water. Ten recirculations were performed per run increasing the oil-to-water ratio from a nominal 1:40,000 up to 1:1,200,000. To ensure that recirculation had no effect on the results, a series of experiments were performed in which clean water was pumped into the system rather than water from the filter. This series of experiments resulted in the same values as the experiments where the water was recirculated.

Figure 4 shows the results of these experiments graphically. The effectiveness values are relatively constant over the oil-to-water ratio measured. In summary, the oil-to-water ratio shows little or no effect on dispersion results when the ratio is 1:1000 or

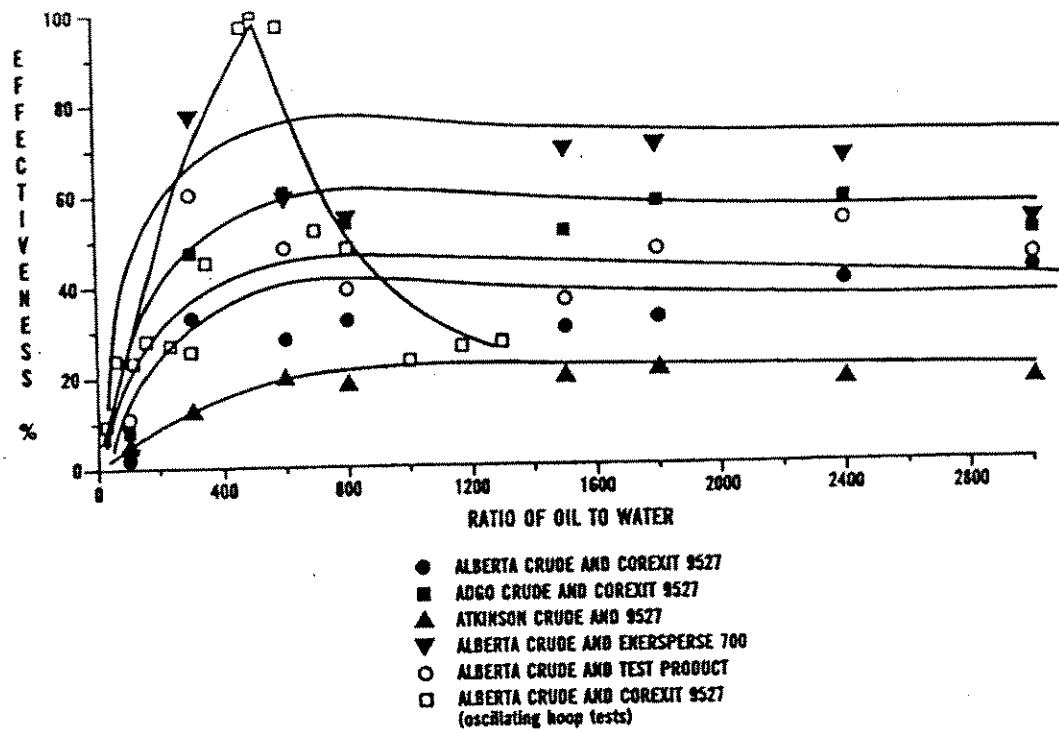


Figure 3. Effect of oil-to-water ratio on effectiveness

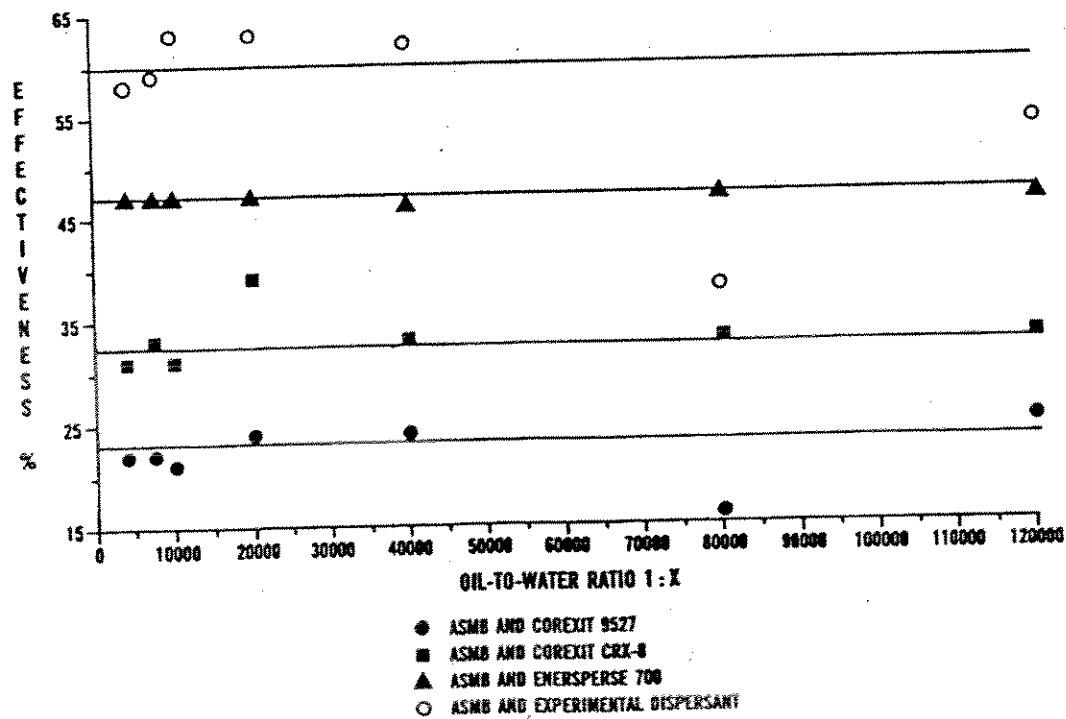


Figure 4. Effect of high oil-to-water ratio on effectiveness

higher, but shows large effects when the ratio is at 1:500 or smaller. At 1:500 effectiveness results are the highest measured and below 1:200 effectiveness values decrease significantly.

The effect of settling time has been investigated with 3 apparatuses. The results for these experiments with the swirling flask are shown in Table 4, with the Mackay apparatus in Table 5 and with the oscillating hoop in Table 6. In all cases, the effect of settling time is highly dependent on the oil-dispersant combination but the effect is the same with each apparatus. An oil-dispersant combination that shows a rapid falloff in effectiveness with time does so in all three tests. The opposite case is also true. The fact that a number of oils (for example; Atkinson, Hibernia and Lago Medio) do show this decrease in effectiveness with increasing settling time indicates that they produce dispersions with larger droplets and are thus unstable. The increase in settling time beyond 10 minutes does not yield significantly different results, as can be seen in Table 4. It is suggested that the 10-minute settling time is optimal for the apparatus tested here.

The effect of settling time is an important factor in the operating protocol of the various effectiveness experiments. The effect can be as much as one order of magnitude for a particular oil-dispersant combination and is repeatable. Furthermore the effect is consistent among different apparatuses.

TABLE 4		EFFECT OF SETTLING TIME IN THE SWIRLING FLASK							
OIL	DISPERSANT	PERCENT DISPERSION AFTER SETTLING TIME IN MINUTES							
		0	2.5	5	7.5	10	12.5	15	20
ASMB	C9527	68	43	37	33	30	30	29	29
	CRX-8	76	53	44	43	34	33	33	31
	EN 700	81	74	74	71	63	61	60	58
ATKINSON	C9527	86	62	55	47	47	41	42	41
NORMAN WELLS	EN 700	98	83	85	69	71	71	70	69
		60	120	240	420				
ASMB	C9527	22	20	12	14				
	CRX-8	28	11	13	10				
	EN 700	43	24	18	16				

Testing of Dispersant/Oil Combinations Using Similar Protocols

A series of tests was conducted to test the hypothesis that the settling time and oil-to water ratio is very important to the outcome of the dispersion effectiveness. Four devices were used, the swirling flask, the flowing column, the Labofina and the Mackay apparatus. Published protocols were adhered to with three exceptions. The oil-to-water ratio was set to 1:1200 in each apparatus except in the case of the flowing cylinder where the minimum is 1:4000. The settling time was set to 10 minutes in all cases except again in the case of the flowing cylinder where this parameter is not relevant. Thirdly, the analysis was performed using the procedure of extracting with methylene chloride, analyzing at three wavelengths and averaging the results. This procedure results in greater accuracy than published procedures where only one wavelength is used.

The results of this comparison testing procedure are shown in Table 7. The tests

TABLE 5

EFFECT OF SETTLING TIME
IN THE MNS APPARATUS

OIL	DISPERSANT	PERCENT DISPERSED AFTER SETTLING		
		NO TIME	5-MINUTE	10-MINUTE
ASMB	C9527	99	88	83
	CRX-8	69	26	21
	EN 700	94	93	91
ATKINSON	C9527	99	31	24
	CRX-8	99	30	23
	EN 700	85	23	16
AVALON	C9527	92	28	22
	CRX-8	85	16	12
	EN 700	74	22	21
FEDERATED	C9527	73	12	7
	CRX-8	91	70	66
	EN 700	95	83	81
HIBERNIA	C9527	100	64	52
	CRX-8	94	30	25
	EN 700	92	38	31
ISSUNGNAK	C9527	100	88	81
	CRX-8	100	92	83
	EN 700	100	93	86
LAGO MEDIO	C9527	20	0	0
	CRX-8	78	22	18
	EN 700	95	28	12
NORMAN WELLS	C9527	100	65	55
	CRX-8	98	77	74
	EN 700	100	90	81
PRUDHOE BAY	C9527	95	43	30
	CRX-8	90	27	22
	EN 700	90	69	67
TRANSMOUNTAIN	C9527	99	82	81
	CRX-8	100	30	23
	EN 700	95	77	70
UVILUK	C9527	94	80	77
	CRX-8	82	45	44
	EN 700	93	91	87

TABLE 6

EFFECT OF SETTLING TIME IN THE OSCILLATING HOOP

OIL	DISPERSANT	PERCENT DISPERSION	
		NO TIME	5-MINUTE
AMAILIGAK	C9527	100	90
	CRX-8	100	56
	EN 700	92	64
ASMB	C9527	51	26
	CRX-8	82	21
	EN 700	91	82
ATKINSON	C9527	92	52
	CRX-8	86	48
	EN 700	86	78
AVALON	C9527	84	40
	CRX-8	87	18
	EN 700	52	16
FEDERATED	C9527	93	33
	CRX-8	62	23
	EN 700	92	54
HIBERNIA	C9527	94	50
	CRX-8	76	65
	EN 700	81	54
ISSUNGNAK	C9527	100	51
	CRX-8	85	7
	EN 700	98	91
LAGO MEDIO	C9527	86	10
	CRX-8	89	64
	EN 700	86	64
NORMAN WELLS	C9527	62	29
	CRX-8	67	17
	EN 700	67	57
PRUDHOE BAY	C9527	92	65
	CRX-8	88	37
	EN 700	84	73
TRANSMOUNTAIN	C9527	84	76
	CRX-8	84	37
	EN 700	84	78
UVILUK	C9527	84	76
	CRX-8	83	45
	EN 700	78	72

were conducted using 16 different oils and three different dispersants, the Exxon products Corexit 9527, CRX-8, and the British Petroleum product Enersperse 700 (formerly known as BP MA-700). As Table 7 shows, the dispersant effectiveness values are nearly identical for the four tests. Oils that are very readily dispersed naturally, that is without the use of dispersant, were measured by a blank run and correcting the dispersion for this effect. Table 7 shows that virtually identical dispersant effectiveness results are produced by all four apparatuses when the oil-to-water ratio is the same at 1:1200, when the settling time is 10 minutes, and when the results from the two energetic devices, the Labofina and Mackay, are corrected for natural dispersion.

The results indicate that laboratory dispersant effectiveness results can be similar even if measured in very different apparatuses. The factors in achieving the same results is the settling time allowed before taking the sample; the oil-to-water ratio and finally, correction for natural dispersion is necessary in the more energetic apparatus.

These findings have extensive implications: first, energy is a prime factor; secondly the fact that effectiveness values tend to one value for a given oil/dispersant combination suggests that this value may have physical implications or meaning; and thirdly, there will be impact on the selection of testing apparatus.

Energy has long been thought to be the most important factor in laboratory dispersant effectiveness testing.^{18,19} It was felt that results could only be correlated with the energy level and that this would have to be measured at sea to give true indication of dispersant effectiveness. For example, one thought that if one could have an energy-measuring device appropriate to oil spill dispersion, one could measure the energy at sea and subsequently in a laboratory device and assign a sea-state equivalent value to this laboratory device, Beaufort 3 as an example. The laboratory measure would then represent dispersion only at that energy level. The four devices used in this study have, by visual examination, widely varying energy levels. The energy levels of the Labofina and Mackay are much higher than that of the swirling flask and the flowing cylinder devices. This is borne out by the fact that one cannot measure natural dispersabilities in either of the latter two devices, irrespective of operating conditions. The observation in this study, that the apparent energy differences in the apparatus could be compensated for, leads one to conclude that energy should be a topic of study.

ACCELERATED WEATHERING

Few studies have been conducted to investigate the changes in oil composition associated with chemical dispersion. Some workers have investigated the accelerated weathering or evaporation attributed to dispersant action, but did not attempt to quantify the effect. Two specific phenomena were investigated; the accelerated weathering caused by dispersants, and secondly the change in the composition of the n-alkanes (the normal or straight-chain aliphatic compounds) which often constitute a large part of the oil's volume. These compounds can be studied by gas chromatography, a technique that makes it easy to identify and quantify them.

Dispersant-accelerated weathering (evaporation) has been noted in the past by several workers. McAuliffe was the first to publish information on this topic.²⁰⁻²² This phenomenon was further defined by McAuliffe in subsequent laboratory experiments where it was found that the C₂ to C₁₀ hydrocarbons under a chemically-dispersed slick were of a lower concentration than under mechanically-dispersed slicks.²³ McAuliffe subsequently reviewed a number of experiments, both field and laboratory, in which the accelerated weathering of C₂ to C₁₀ hydrocarbons was measured.²³ Wilson and co-

Table 7

Comparison of Disperability in Four Apparatuses

OIL	DISPERSANT	DISPERSABILITY IN PERCENT			
		SWIRLING FLASK	FLOWING CYLINDER	LABOFINA	MNS
ADGO	9527	61	52	78	64
	CRX-8	42	40	77	87
	EN 700	67	59	76	93
AMAILIGAK	9527	48	38	86	44
	CRX-8	56	46	73	85
	EN 700	54	39	59	73
ASMB	9527	22	21	31	39
	CRX-8	28	31	34	61
	EN 700	43	43	62	76
ATKINSON	9527	7	18	57	17
	CRX-8	9	10	47	19
	EN 700	8	18	55	22
BENT HORN	9527	29	46	29	29
	CRX-8	27	37	27	51
	EN 700	44	51	19	42
FEDERATED	9527	39	35	51	35
	CRX-8	23	31	35	76
	EN 700	38	42	70	76
GEAR OIL	9527	29	18	18	12
	CRX-8	40	25	27	10
	EN 700	10	6	15	30
HIBERNIA	9527	6	12	23	6
	CRX-8	9	10	19	9
	EN 700	7	8	23	14
ISSUNGNAK	9527	24	22	61	41
	CRX-8	42	76	35	100
	EN 700	42	60	75	100
LAGO MEDIO	9527	7	8	29	16
	CRX-8	11	15	19	19
	EN 700	10	23	24	27
LUBE OIL	9527	13	19	40	44
	CRX-8	14	24	40	53
	EN 700	13	23	40	80
MOUSSE MIX	9527	9	15	27	30
	CRX-8	11	25	18	26
	EN 700	24	32	23	43
NORMAN WELLS	9527	41	55	65	47
	CRX-8	60	47	70	65
	EN 700	63	53	74	89
PANUK	9527	100	100	89	100
	CRX-8	93	100	85	100
	EN 700	100	100	87	100
PRUDHOE BAY	9527	7	13	47	27
	CRX-8	5	16	38	23
	EN 700	17	14	48	37
SYNTHETIC CRUDE	9527	57	50	78	83
	CRX-8	69	55	40	91
	EN 700	61	39	76	88

LEGEND 9527= COREXIT 9527, CRX-8= COREXIT CRX-8, EN 700= ENERSPERSE 700

workers conducted extensive tank experiments and noted a slightly-faster evaporation rate for chemically-treated oil.²⁴ Anderson and co-workers noted major differences in the toxicity to shrimp of mechanically and chemically-dispersed oil.^{25,26} Further studies showed that the lower toxicity of chemically-dispersed oil was due to accelerated evaporation of toxic mono-aromatics. Bowler and co-workers conducted a number of experiments using a laboratory effectiveness apparatus and found that dispersants increased the evaporation rate of oil when comparing treated and untreated oil.²⁷ Fingas and co-workers found similar accelerated weathering using dispersants on fuel in a model sewer system.^{28,29}

Experimental

Evaporative loss was measured in laboratory dispersant effectiveness apparatus. Three different apparatuses were used. The swirling flask apparatus was operated according to published procedure.¹³ The MNS (Mackay-Nadeau-Steelman) or Mackay test was operated according to published procedure except that the oil-to-water ratio was maintained at 1:1200.¹⁴ The Warren Springs, Labofina or alternatively, the rolling flask test, was also operated according to published procedure except for the same oil-to-water ratio as above.²³ The same oil-to-water ratio was maintained in all apparatus to eliminate this as a variable and also for the reason that lower ratios have been shown to affect results. The full experiments and results are in the literature.¹³

All experiments were run in the same manner; oil was applied to the water surface, the apparatus energized in its regular manner and after the run was completed, the surface oil was removed using 2.5 cm by 2.5 cm sorbent pads (SPC sorbent). These were in turn extracted using 30 mL methylene chloride. Concentrations were determined colorimetrically using a previously-prepared calibration curve. The calibration curves were prepared in analogous fashion to ensure that losses and sorbent efficiencies were accounted for. Results were repeatable to within 10%. The untreated crude oil was processed in the same manner as above to ensure that evaporation was compensated for. To account for accelerated weathering, experiments were done to measure the oil remaining on the surface and that in the water column. The amount lost to accelerated weathering was obtained by subtracting those amounts from the original amount added. The initial or untreated oil quantity was determined to be that amount left after processing in the apparatus without dispersants. This was done to ensure that losses, evaporation and inefficiencies were accounted for. The oil left on top after dispersion was determined using the sorbent procedure described above. Oil in the water column was determined by the published procedure for the apparatus and always involved extracting a portion of the oil and analyzing colorimetrically using a predetermined standard curve. At least two runs were performed for every apparatus, oil and dispersant combination. If values were outside 15%, the experiments were repeated until the majority of values were within 15% of each other.

Five oils were used in both experiments. Mousse mix is a name given to a mixture of Bunker C and Alberta Sweet Mixed Blend (ASMB) and is frequently used in our laboratory for physical experiments. The name derives from the high tendency of that mixture to form mousse (water-in-oil emulsion).

The results of the experiments are summarized in Table 8. The values presented in this table are the amounts of oil unaccounted for after the oil on the surface and in the water column were computed, and thus represent the amount lost through evaporation since other losses were compensated for during the calibration procedures.

The accelerated weathering ranges from 0 to 30 % with an average of 11 %. These values should be taken in context with the error for each of the apparatus used; swirling flask 5%, Labofina 7%, and MNS 10%. All weathering values obtained were positive, thus indicating that despite the measurement error, dispersants always accelerate the weathering of the oil. The accelerated weathering is least in the MNS, as one might expect because the device operates with a high velocity stream of air and this would evaporate the untreated oil to a large extent. If the untreated oil is evaporated to a large extent the loss by accelerated weathering is small, because results are always compared to the weathering of this untreated oil after processing through the entire experiment. These results indicate that an average of 11% of the mass is removed over a short time by the action of dispersants. Untreated oil would ultimately lose this mass by evaporation over a longer time depending on temperature and wind speed.

Table 8

EVAPORATION IN THREE APPARATUS

		PERCENTAGE EVAPORATION IN APPARATUS			
OIL	DISPERSANT	SWIRLING FLASK	LABOFINA	MNS	AVERAGE
ADGO	COREXIT	4	0	0	1
	ENERSPERSE	0	2	3	2
ASMB	COREXIT	25	31	2	19
	ENERSPERSE	11	25	7	14
MOUSSE MIX	COREXIT	15	6	2	8
	ENERSPERSE	9	8	14	10
HIBERNIA	COREXIT	30	18	10	19
	ENERSPERSE	25	4	14	14
LAGO MEDIO	COREXIT	4	3	12	6
	ENERSPERSE	30	12	2	15
Overall					11

This effect, although significant, is not major and does not dominate the dispersion process. These findings do however, have implications for dispersant laboratory testing. These effects must be known if the top or remaining portion of the oil is to be analyzed. The application of remote sensing or other surface techniques, to measure oil dispersion on the sea should include consideration of the additional amount removed by accelerated weathering.

METHODS OF ANALYSIS

The results of some tests conducted in the past years appeared to be in error and the problem was investigated. It was found that some surfactants, in particular an experimental dispersant known as BQ, produced a high degree of coloration in the extraction process. This coloration, because of the methodology used to measure effectiveness, interferes and causes the values to appear quite high. The traditional method of measuring laboratory dispersant effectiveness is to take a small aliquot of the dispersion test water, extract the oil, usually with methylene chloride and then measure

the colour at a specific wavelength. This value is compared to a standard curve and an effectiveness assigned. The preparation of the standard curve was traditionally done by injecting the appropriate amount of oil directly into the methylene chloride and measuring colour density. When the swirling flask test was developed, it was found that the traditional approach of preparing standard curves was somewhat in error because the simple addition of water to the extraction process produced some coloration in the methylene chloride. This results in inflated effectiveness values. The protocol for the swirling flask effectiveness attempts to compensate for this error by using a standardization procedure that is directly analogous to the actual extraction procedure. This cancels the effect that sea water alone can have on the results. Also, the protocol calls for colorimetric measurements at three separate wavelengths (340, 370 and 400 nm) to overcome errors caused by the lack of resolution of the spectrometer.

The effect of the dispersant on the calibration procedure was tested but was not included because the commercial dispersants tested did not show a significant effect. However, the re-investigation of this in recent times has shown that some surfactant mixtures will result in high coloration of the methylene chloride causing high and incorrect dispersant effectiveness values. Table 9 gives summary values of some experiments conducted to investigate calibration procedure.

Table 9 EFFECT OF CALIBRATION PROCEDURES ON EFFECTIVENESS VALUES

Oil/Dispersant Combination	EFFECTIVENESS IN PERCENT AS GIVEN BY EACH CALIBRATION PROCEDURE			
	TRADITIONAL (direct oil)	STANDARD (water corrected)	STANDARD + (water & dispers.)	CORRECTION (dispersant alone)
ASMB + BQ	60	46	29	27
ASMB + Corexit	33	31	33	
Issungnak + BQ	65	46	21	22
Issungnak + Corexit	22	22		
Norman Wells + BQ	75	57	31	33
Syncrude + BQ	40	27	30	

The means for performing each form of calibration is as follows. The "traditional" method, not generally used by Environment Canada, consists of adding the correct amount of oil directly to the extract, usually methylene chloride. The method does not compensate for coloration caused by the sea water or the dispersant. The "standard" method refers to the method published for the swirling flask apparatus in which the standard curves are prepared in a manner analogous to the actual extraction procedure. This method compensates for the coloration caused by the water and losses incurred during the extraction procedure. The next method given in Table 9 is referred to as "standard +" and consists of applying the standard procedure plus adding the dispersant premixed in proportion to the actual test (1:25, dispersant to oil). This method directly compensates for dispersant coloration but would require that a complete calibration curve be prepared for every oil/dispersant combination. The final method is to correct the standard curve by compensating for the dispersant. This is accomplished by running a calibration experiment without oil but with the dispersant. Colorimetric readings are taken and subtracted from the ultimate experimental results. This method has the advantage that a correction is achieved for each dispersant without having to draw up an entire calibration curve. As can be seen from the table, this method yields results similar to the procedure of preparing an entire calibration curve but is much simpler.

The results in Table 9 show that the dispersant BQ yields much higher dispersant

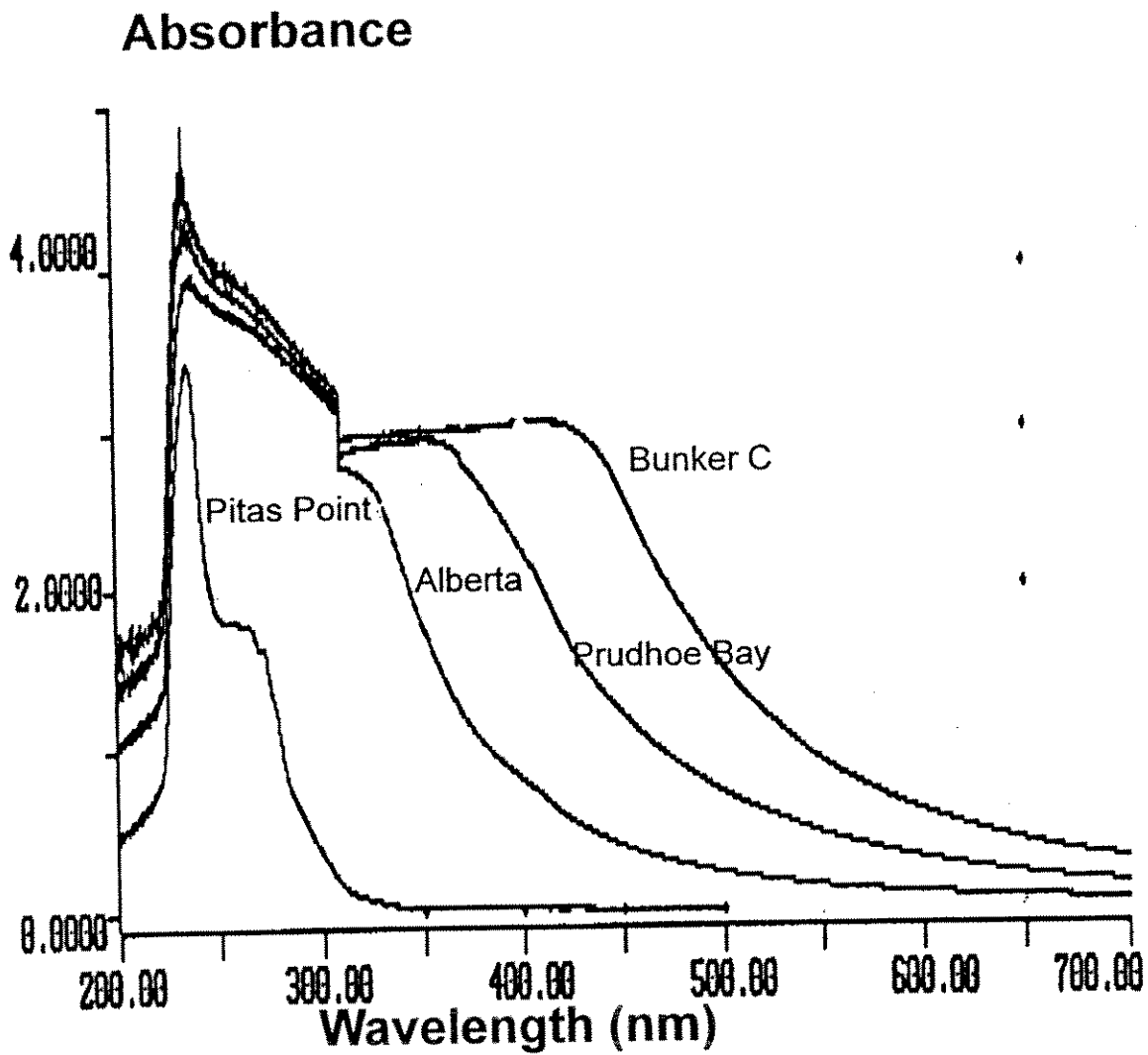
effectiveness than is correct. The dispersant BQ requires correction for the coloration it produces by itself. The dispersant Corexit 9527 does not appear to yield such errors. The few values done by the traditional method indicate that this does not yield satisfactory results because large amounts of coloration are not compensated for. Given that a dispersant itself can be run through the calibration procedure and a correction value derived, this procedure should be followed with all new dispersants to ensure that true effectiveness values are measured.

A second round of experiments was conducted to investigate the problem further. Sample extracts of the methylene chloride were analyzed both by the colorimetric method and by gas chromatography. The gas chromatograph was a Hewlett Packard 5890, Series II. The column was a 30 m x 0.32 m ID DB-5 fused silica, 0.25 μ film thickness. The detector was a FID (Flame Ionization Detector). The inlet was a split/splitless inlet operated in the splitless mode and the unit was equipped with a Hewlett Packard 7673 autosampler. The carrier gas was helium, 2.5 mL/min and the make-up gas was also helium at 27.5 mL/min. The flow rate for hydrogen was 30 mL/min and for air 400 mL/min. The injection volume was 1 μ L. Injector temperature was 280 °C and the detector temperature was 300 °C. The temperature program was 50 °C for 2 min, then 5 °C/min to 300 °C held for 16.33 min. The total run time was 60 minutes. An alkane standard mixture from C₈ to n-C₃₀, including pristane, o-terphenyl and 5-d-androstane, was used daily to calibrate the procedure.

Two oils were used in this test - Alberta Sweet Mixed Blend and Pitas Point. The latter oil is particularly troublesome since it has a low absorption coefficient. Typical colorimetric analyses of dispersion tests yield results as high as 350 % with Pitas Point. The results of the dual analysis are presented in Table 10. The visible absorption spectra of several oils are shown in Figure 5. This shows that light oils, such as Pitas Point, have low absorbance at the typical wavelengths chosen. This figure also illustrates the importance of selecting wavelength correctly for different oils. The change in absorbance is very sharp in the lower wavelength regions. This implies that a small inaccuracy in wavelength of the spectrometer can result in a significant change in the absorbance and consequently a large variation in effectiveness. Since the cost of gas chromatographs and visible spectrometers are becoming increasingly similar, it is suggested that one may wish to switch to a chromatographic method to avoid these very large errors.

Table 10		Comparative Analysis by GC and Colorimetry		
Oil	Dispersant	Effectiveness in Percent		Standard Deviation
		Average Effectiveness Using Gas Chromatography	Average Effectiveness Using Colorimetry	
Alberta Sweet Mixed Blend	BQ	33	67	10.9
	Corexit 9527	33	39	22
Pitas Point	Corexit 9527	39.6	178	19.3
	Enersperse 700	49.5	156	11.8

**Figure 5 Comparison Of the Absorbance
of Different Oils**



Test results for high wax content oils show that these require special extraction procedures to yield consistent results. Waxes have poor solubility in methylene chloride and require a mixture of solvents, such as methylene chloride and pentane, to be fully extracted and not cause the formation of a white precipitate which gives high and unrepeatable values. Tests conducted in the laboratory show that a mixture of 20% pentane in dichloromethane will extract the waxes and result in a more reasonable value.

EFFECT OF SALINITY

The effects of water salinity were tested using the swirling flask apparatus operated in a normal configuration (see appendix) and using standard procedures except for changes in the parameter of interest. Dispersant was pre-mixed with the oil to ensure a higher degree of repeatability. Experiments were performed with Alberta Sweet Mixed Blend (ASMB) crude oil and the dispersant Corexit 9527, except where noted.

The effect of salinity on dispersant effectiveness was tested using Alberta Sweet Mixed Blend, Norman Wells and Adgo crude oils with the dispersants Corexit 9527 and Enersperse 700 and Citrikleen. These results are shown in Figure 6. Polynomial curves with two variables were fit to the data using a least-squares procedure. The results are consistent between the different oil/dispersant combinations. Dispersant effectiveness is at a maximum at a salinity of 40 to 45 ‰ (parts-per-thousand or degrees salinity) and falls down very sharply with a decrease or increase in salinity. Freshwater effectiveness is low for all oil/dispersant combinations. Separate experiments were conducted with other dispersants, including those designed for freshwater with similar results. This indicates that ionic interaction is necessary for the dispersion process, at least for the dispersants tested. Dispersant laboratory tests should use salt water with salinity corresponding to that expected in actual usage.

THE EFFECT OF ENERGY

Several rounds of experiments were conducted to determine the effect of varying energy. Several oils were used in these tests. Table 11 lists these oils and gives their basic physical properties.³⁰ The dispersants used in this study are the Exxon product Corexit 9527 (abbreviated "C9527" in some tables in this paper) and the Dasic product Dasic Slickgone LTS (abbreviated "Dasic" in this paper). All runs where dispersant was used, were performed with dispersant already mixed in the oil at a ratio of 1 to 25 by volume. This practice was adopted to achieve more repeatable results as determined in earlier experiments where both premixed and drop-wise additions were used.³¹ Saltwater was prepared with sodium chloride to 33 ‰ or degrees salinity. All tests were done at a temperature of 20 °C. Apparatus, and the oil and water were left at these temperatures for at least 20 minutes before the beginning of each test to ensure thermal equilibrium. All tests were done in thermally-controlled chambers.

**FIGURE 6 VARIATION OF EFFECTIVENESS
WITH SALINITY**

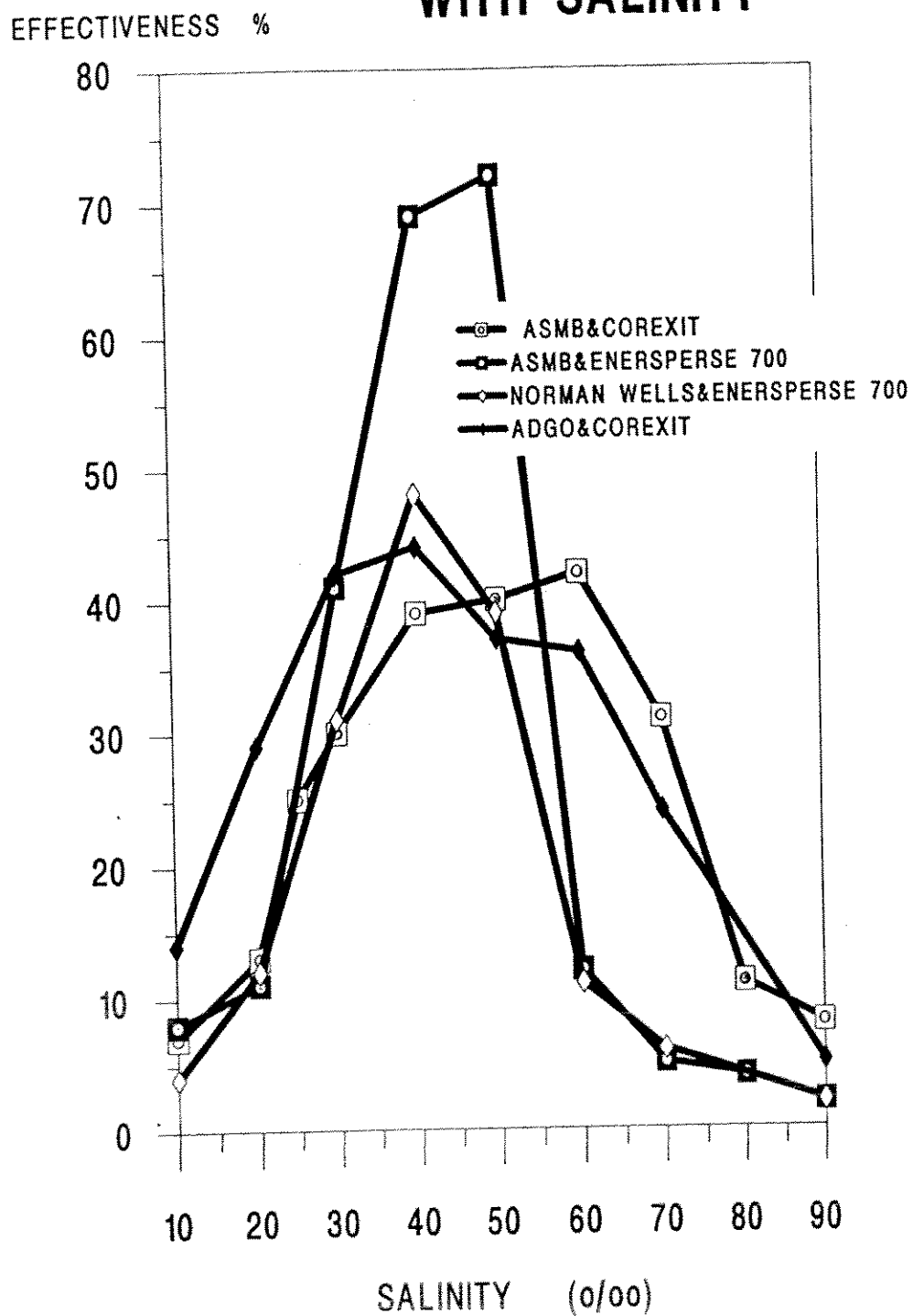


TABLE 11		TEST OIL PROPERTIES	
OIL	DESCRIPTION	KINEMATIC VISCOSITY (mm ² /s at 15 °C)	DENSITY (g/mL at 15 °C)
ASMB	ALBERTA SWEET MIXED BLEND	8	0.84
ARABIAN LIGHT	ARAB BLEND	40	0.87
ARABIAN HEAVY	ARABIAN BLEND	45	0.89
BUNKER C LIGHT	LESS-VISCOUS BUNKER C	200	0.93
ENDICOTT	COOK INLET CRUDE	85	0.91
MALONGO	ANGOLAN CRUDE OIL	100	0.88
NORTH SLOPE	PRUDHOE BAY CRUDE	55	0.88

An apparatus, called simply "the high energy test" in our laboratories, was developed to measure dispersion at very high energy levels. This vessel is square and of dimensions 30 cm on all sides. The effect of the corners is to create high levels of turbulence. The volumes of oil and water used are 0.25 mL and 5 L to yield an oil-to-water ratio of 1:20,000. This ratio was shown in a previous paper to yield repeatable results.³² The mixing time is 20 minutes and the settling time is 10 minutes before samples are taken. The mixing energy is supplied by a Brunswick shaker, a moving table apparatus. This shaker is capable of rotational speed variations from 50 to 440 rpm with relatively good repeatability. The revolution meter on the shaker is calibrated periodically with a tachometer to ensure accuracy. A pipette is used to remove a 30 mL sample from the apparatus after the settling time.

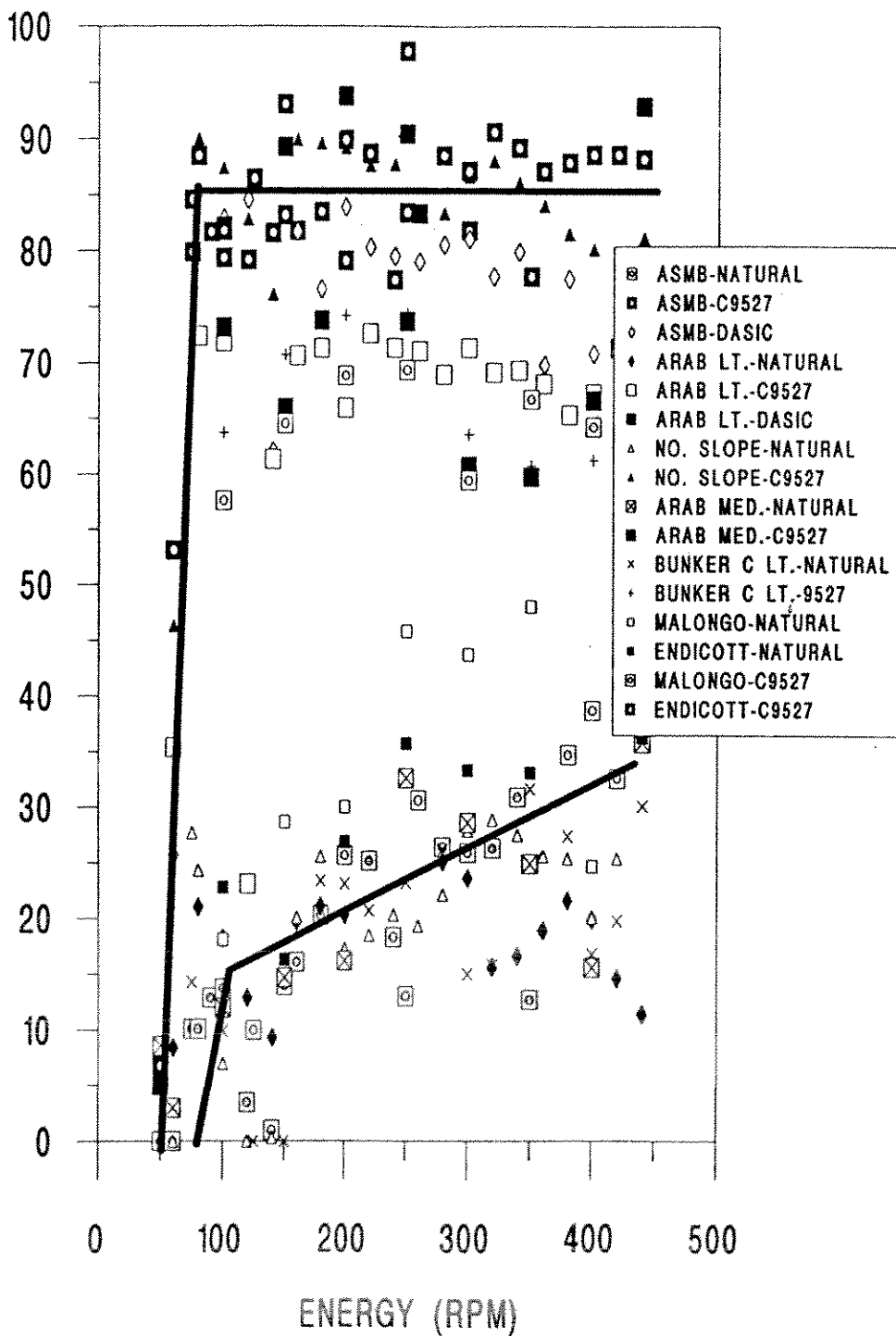
Analysis is performed by taking a sample of water from the test vessel after the run is complete, extracting the water with a solvent and measuring the absorbance at three visible wavelengths (340, 370 and 400 nm), and then assigning effectiveness on the basis of a calibration curve. Calibration curves are prepared in a manner similar to the actual runs. Water is used in these calibration runs to ensure that extraction efficiency is compensated for and to account for the coloration caused by small water droplets alone.

The "high energy apparatus" was tested for validity by constructing two other apparatuses with different vessels. Tests were done in all three apparatuses to ensure that the data showed no artifacts associated with the type of vessel employed, the volume of water, the oil-to-water ratio and the type of agitation. These results have already been reported in the literature.³²⁻³³ All three test apparatuses yielded similar data.

Results are summarized in Figure 7. This figure illustrates the results of dozens of experiments. The lines on the graph are applied to show the overall tendency of the

FIGURE 7 COMPOSITE DATA FROM THE HIGH ENERGY EXPERIMENTS

EFFECTIVENESS
%



data. The findings are as follows: that dispersion increases very rapidly from a low value to nearly 80 or 90% and that natural dispersion onset occurs at an energy level similar to or higher than that for chemical dispersion, and finally, that the natural dispersion curve has a lesser slope than that for chemical dispersion. The energy is sufficient in the high energy apparatus to disperse Bunker C light. Regular Bunker C will not disperse chemically or naturally in this apparatus. During the natural dispersion runs and partially during the chemical runs, the Bunker C grouped into large droplets on the surface. This indicates that the energy in the apparatus is insufficient to disperse this oil or that this oil is undispersable under test conditions. Onsets of natural dispersion are difficult to assign, but are the same or lag the chemical dispersion. The curves of natural dispersion have a lesser slope than those for chemical dispersion. In addition, the heavier oils tested are not dispersed to the same degree as other oils. The effect of chemical dispersant is to increase the dispersion amount by a large factor for the same level of mixing energy.

The high-energy dispersion of oil is difficult to measure because of the high noise level in the data. As the average energy increases so too does the amount of different energy levels, thus causing noise in the data. The natural and chemical curves were tested for fit with a variety of functions in a previous paper.³² The conclusion of this paper was that both were best fit with linear functions. The chemically-dispersed oil data was addressed by applying linear regression to the onset portion and then standard statistics to the top or "saturated" portion of the graph. The onset of the "natural" dispersion curves are very difficult to assign and in Figure 7 are shown as linear, although the shape may be the same as that of the chemically-dispersed oil. Further discussion on statistical methods is found in a previous paper.¹⁵

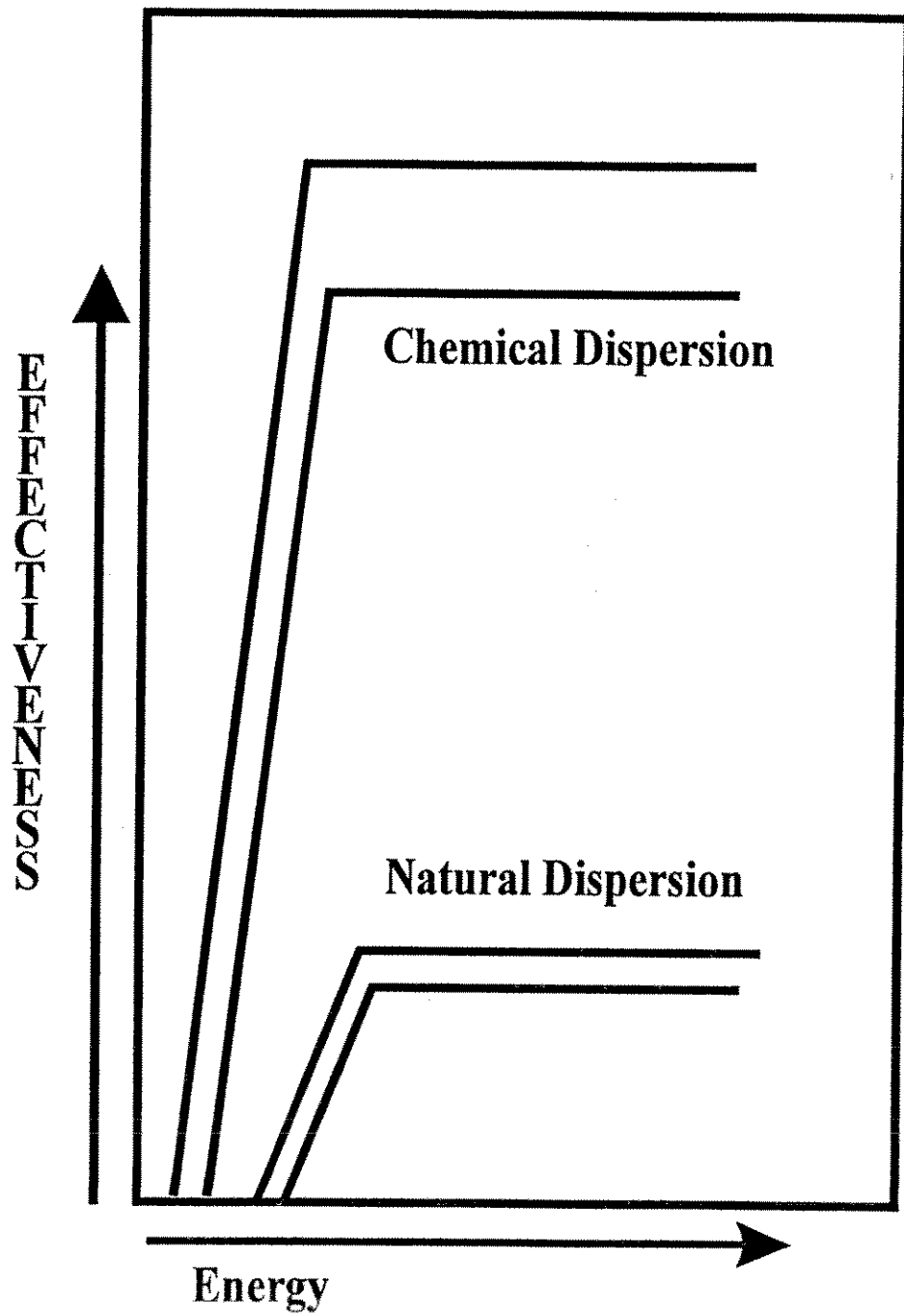
The general trend of the data is shown in Figure 8. Chemical dispersion shows a rapid onset with energy to a high value and then remains relatively constant with increasing energy. Natural dispersion onsets are difficult to establish, however appear to be higher than their chemical equivalents. The slope of the natural dispersion curve for a given oil is much smaller than its chemical dispersion counterpart. The natural dispersion curve is approximately linear.

Chemical dispersion increases with energy (measured in these experiments as the number revolutions of the experimental apparatus in a given time period) in a linear fashion until a maximum is reached. For light oils this maximum is about 80%. For heavier oils this is about 65%. The dispersion curve is very steep, that is only a small amount of energy causes a large amount of change in dispersion level. There exists an energy threshold below which little dispersion occurs. Chemical dispersion curves for different oils appear to be parallel (have similar slopes). This indicates that the mechanism is fixed and that only the threshold varies.

Natural dispersion is analogous to chemical dispersion except that the increase with energy is much less. The onset of natural dispersion is difficult to assign but is similar to, or higher than, that of chemical dispersion.

The major question these experiments raise is how the energy in these tests relates to that prevailing at sea. There are a few observations which indicate that most typical sea energies actually occur at the low end of the energy range shown in the test data presented here. In one test at sea, ASMB and light Bunker C were observed to start dispersing naturally at a sea state of Beaufort 6.³² The EKOFISK BRAVO oil was observed to disperse naturally at sea states around Beaufort 5 or 6.³³⁻³⁴ It is recognized

Figure 8 Schematic High Energy Results



that turbulent energy is the important factor for dispersion. Technology does not exist at this time to measure this type of energy at sea nor in the laboratory.

This study has a number of implications for laboratory testing of dispersants. First, energy level in apparatus is a crucial factor. Many laboratory apparatuses appear to have energy far exceeding that found in most sea conditions and thus may not be representative tests. Furthermore, since energy is such a significant variable, efforts should be made to ensure that any particular apparatus is maintained at a constant energy and that the oil/water system is not subject to short high-energy bursts such as an acceleration at the start of agitation. Energy is a very important factor in yielding consistent results. The final point is the correction for natural dispersion in laboratory tests. The tests described above indicated that one could correct for energy by subtracting the natural dispersion amount. Although this seems to work in actual practice, questions can be raised because the shape of the curve at the threshold is uncertain and because the slope of the line is different for natural dispersion - indicating a somewhat different process.

OPTIMUM OIL-TO-WATER RATIOS FOR NATURAL DISPERSION

A study of the effect of oil-to-water ratio on amount of oil in the water was conducted using 2 different experimental apparatus and procedures. The percent of oil in the water column (naturally dispersed) increases as the oil-to-water ratio increases up to about 1:20,000. This is very different from the chemically-dispersed situation where the same inflection point is about 1:600. Full data are in the literature.³²

This implies that laboratory apparatuses with low oil-to-water ratios should not be used to measure the dispersability of oils.

SUMMARY AND CONCLUSIONS

The results of the above studies can be summarized as follows:

1. It is important that laboratory tests be designed for their prime purpose. This could be screening of effective products or physical studies. Laboratory tests around the world, although different, do generally yield similar rankings of dispersant effectiveness for a given oil. A major concern is correspondence to reality, however, "real" conditions such as sea energy have not been measured either.
2. A major concern in laboratory tests is the "wall effect". Testing in this laboratory on four apparatuses, the swirling flask, MNS, Labofina and the high energy test, has shown that the losses to the walls in the latter two tests are very significant. The oil contact with the swirling flask wall is minimal. Wall effect can show up as decreasing dispersion or effectiveness with increasing time.
3. The oil-to-water ratio in lab tests is important. Data show that oil:water ratios below 1:500 yield anomalous results. For natural dispersion, the oil-to-water ratio must be above 1:20,000 to avoid droplet interaction.
4. The settling time or quiescence time, in laboratory tests has been shown to be an important factor. Studies show that for small laboratory apparatus a time of at least 10 minutes is required to cream the large unstable particles. The remaining droplets do correspond in size and concentration to those measured at sea, indicating that the settling procedure is valid.

5. It has been shown that the effectiveness results from four apparatuses can be nearly identical if the oil-to-water is adjusted to above 1:500; if the settling time is at least 10 minutes and if the high energy devices are corrected by blanks - ie. effectiveness results with oil and no dispersant.

6. Accelerated weathering occurs after dispersant application. The loss varies with oil type but can be 10 to 40%. This implies that use of the remaining oil on the surface is not an accurate means to measure oil dispersion.

7. There exist several problems in measuring the oil content in water using colorimetry. With light and waxy oils the effectiveness is exaggerated as much as 700%. The effectiveness is always exaggerated using many of the published procedures. Medium crude oils can be evaluated with reasonable accuracy if the calibration curves are made using analogous procedures to the test itself - ie. using water and the dispersant. Light crude oils cannot be measured accurately using colorimetric methods. Heavy crude oils are problematic. Waxy oils require the use of a mixed extractant of 20% pentane in dichloromethane to yield accurate results.

8. Salinity of the test water can be an important factor. The dispersants tested in this study are most effective at a salinity of about 40 ‰ (ppt or degrees salinity). Dispersant effectiveness rapidly decreases when salinity is increased or decreased. Freshwater effectiveness of present-day dispersants is very low.

9. Energy level is important to dispersant effectiveness results. There exists an energy threshold above which oils are dispersed to a large degree in water. The energy levels at which these thresholds occur is very high even for light crude oils and may exceed the high energies sometimes observed at sea. Many laboratory apparatuses have very high energy levels and exceed the energy threshold for natural dispersion. It is suggested that this results in problems in repeatability and correspondence to actual sea conditions.

REFERENCES

- 1 Fingas, M.F., M.A. Bobra and R.K. Velicogna, "Laboratory Studies on The Chemical and Natural Dispersability of Oil", in *Proceedings of the 1987 Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 241-246, 1987.
- 2 Byford, D.C. and P.J. Green, "A View of the Mackay and Labofina Laboratory Tests For Assessing Dispersant Effectiveness With Regard to Performance At Sea", in *Oil Spill Chemical Dispersants: Research, Experience and Recommendations*, Tom E. Allen, Ed. STP 840. American Society for Testing and Materials, Philadelphia, Pa., pp. 69-86, 1984.
- 3 Daling, P.S. and H. Nes, "Laboratory Effectiveness Testing of Dispersants: Correlation Studies Between Two Test Methods", poster session presented at Arctic and Marine Oilspill Program Technical Seminar held in Edmonton, Alberta, 3 p., 1986.

- 4 Desmarquest, J-P, J. Croquette, F. Merlin, C. Bocard, G. Castaing and C. Gatellier, "Recent Advances in Dispersant Effectiveness Evaluation: Experimental and Field Aspects", in *Proceedings of the 1985 Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 445-451, 1985.
- 5 Meeks, D.G., "A View of The Laboratory Testing and Assessment of Oil Spill Dispersant Efficiency", in *Proceedings of the 1981 Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 19-25, 1981.
- 6 Nes, H., *Effectiveness of Oil Dispersants: Laboratory Tests*, PFO Project Report No. 1410, Trondheim, Norway, 1984.
- 7 Nes, H. and S. Norland, "Effectiveness and Toxicity of Oil Dispersants", in *Proceedings of the Sixth Annual Arctic and Marine Oilspill Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 132-139, 1983.
- 8 Rewick, R.T., K.A. Sabo, J. Gates, J.H. Smith and L.T. McCarthy, jr., "An Evaluation of Oil Spill Dispersant Testing Requirements", in *Proceedings of the 1981 Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 5-10, 1981.
- 9 Tramier, B., R.D. Cowin, A.H. Edwards, A. Gillot, A. Lewis, J.K. Rudd and J.N. Chavanne, *Oil Spill Dispersant Efficiency Testing: Review and Practical Experience*, CONCAWE Report no 86/52, The Haag, Netherlands, 54 p., 1986.
- 10 Payne, J.R. and C.R. Phillips, *An Evaluation of laboratory and At-Sea Field Testing of Dispersant Effectiveness*, Background Paper Prepared for the Marine Board, Science Applications International, La Jolla, California, 57 p., 1986.
- 11 Clayton, J.R., J.R. Payne and J.S. Farlow, *Oil Spill Dispersants: Mechanisms of Action and Laboratory Tests*, CRC Press, Boca Raton, FL., 103 pp., 1993.
- 12 Daling, P.S. and I.K. Almas, *Description of Laboratory Methods in Part 1 of the DIWO-Project - A Technical Report*, DIWO Report Number 2, SINTEF, Trondheim, Norway, 46 p., 1988.
- 13 Fingas, M.F., D.L. Munn, B. White, R.G. Stoodley, and I.D. Crerar, "Laboratory Testing of Dispersant Effectiveness: The Importance of Oil-To-Water Ratio and Settling Time", in *Proceedings of the 1989 Oil Spill Conference*, American Petroleum Institute, Washington, D.C., p. 365-373, 1989.
- 14 Martinelli, F.N., "The Status of Warren Springs Laboratory's Rolling Flask Test", *Oil Spill Chemical Dispersants: Research, Experience, and Recommendations*, T.E. Allen, Ed., STP 840, American Society for Testing and Materials, Philadelphia, pp. 55-68, 1984.

- 15 Fingas, M.F., D.A. Kyle, J.B. Holmes and E.J. Tennyson, "The Effectiveness of Dispersants; Variation With Energy", in *Proceedings of the 1993 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 567-572. 1993.
- 16 Mackay, D., A. Chau., and K. Hossein, "Effectiveness of Chemical Dispersants: A Discussion of Recent Progress", in *Proceedings of The Sixth Arctic Marine Oilspill Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 151-153, 1983.
- 17 Anonymous, *Guidelines on The Use and Acceptability of Oil Spill Dispersants, 2nd Edition*, Report No. EPS 1-EP-84-1, Environment Canada, Ottawa, 68p. 1984.
- 18 Fingas, M.F., "Dispersant Effectiveness at Sea: A Hypothesis to Explain Current Problems with Effectiveness", in *Proceedings of The Eleventh Arctic and Marine Oilspill Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 455-480, 1988.
- 19 Chau, A., Sproule, J., and D. Mackay, *A Study of the Fundamental Mechanism of Chemical Dispersion of Oil Spills*, Report No. EE-81, Environment Canada, Ottawa, Ontario, 78 p, 1987.
- 20 McAuliffe, C.D., "Evaporation and Solution of C₂ to C₁₀ Hydrocarbons from Crude Oil on the Sea Surface", in *Fate and Effects of Petroleum Hydrocarbons in Marine Ecosystems and Organisms*, D.A. Wolfe, editor, Pergamon Press, New York, p. 363-372, 1977.
- 21 McAuliffe, C.D., "Dispersal and Alteration of Oil Discharged on a Water Surface", in *Fate and Effects of Petroleum Hydrocarbons in Marine Ecosystems and Organisms*, D.A. Wolfe, editor, Pergamon Press, New York, p. 19-35, 1977.
- 22 Johnson, J.C., C.D. McAuliffe and R.A. Brown, "Physical and Chemical Behaviour of Small Crude Oil Slicks on the Ocean", in *Chemical Dispersants for The Control of Oil Spills*, ASTM STP 659, L.T. McCarthy, Jr., G.P. Lindblom and H.F. Walter, Eds., American Society for Testing and Materials, Philadelphia, p. 141-159, 1978.
- 23 McAuliffe, C.D., J.C. Johnson, S.H. Greene, G.P. Canevari and T.D. Searl, "Dispersion and Weathering of Chemically Treated Crude Oils on The Ocean", *Environmental Science and Technology*, Vol. 14, p. 1509-1518, 1980.
- 24 Wilson, M.P. et al., *Assessment of Treated Versus Untreated Oil Slicks; Final Report*, No. DOE/EV/04047-T3, Department of Energy, Washington, D.C., 348p, 1981.

- 25 Anderson, J.W. S.L. Kiesser, R.M. Bean, R.G. Riley and B.L. Thomas, "Toxicity of Chemically Dispersed Oil to Shrimp Exposed to Constant and Decreasing Concentrations in A Flowing Stream", *Proceedings of The 1981 Oil Spill Conference*, American Petroleum Institute, Washington, D.C., p. 69-75, 1981.
- 26 Anderson, J.W., R. Riley, S. Kiesser and J. Gurtisen, "Toxicity of Dispersed and Undispersed Prudhoe Bay Crude Oil Fractions to Shrimp and Fish", *Proceedings of The 1987 Oil Spill Conference*, American Petroleum Institute, Washington, D.C., p. 235-240, 1987.
- 27 Bowler, B., A. Knapstad, A. Due and M. Sandstad, *Laboratory Studies on the Effect of Oil Dispersant on Evaporation and Dissolution*, SINTEF Report No. 8.096, Trondheim, Norway, 79 p., 1985.
- 28 Fingas, M.F., K.A. Hughes and A.M. Bobra, "The Behaviour of Dispersed and Non-Dispersed Fuels in A Sewer System", in *Oil Dispersants: New Ecological Approaches*, ASTM STP 1018, L. Michael Flaherty, Ed., American Society For Testing and Materials, Philadelphia, p. 274-289, 1989.
- 29 Fingas, M.F., K.A. Hughes and A.M. Bobra, "Fuels in Sewers: Behaviour and Countermeasures", *Journal of Hazardous Materials*, Vol. 19, p. 289-302, 1988.
- 30 Whitarcar, S., M. Bobra, M.F. Fingas, P. Jokuty, P. Liuzzo, S. Callaghan, F. Ackerman and J. Cao, *A Catalogue of Crude Oil and Oil Product Properties (1992 Edition)*, Environment Canada Manuscript Report Number EE-144, Ottawa, Ontario, 643 p., 1993.
- 31 Fingas, M.F., V.M. Dufort, K.A. Hughes, M.A. Bobra and L.V. Duggan, "Laboratory Studies on Oil Spill Dispersants", *Chemical Dispersants - New Ecological Approaches*, M. Flaherty, Ed., ASTM STP 1084, American Society For Testing and Materials, Philadelphia, pp. 207-219, 1989.
- 32 Fingas, M.F., D.A. Kyle, I.D. Bier, A. Lukose and E.J. Tennyson, "Physical and Chemical Studies on Oil Spill Dispersants: The Effect of Energy", in *Proceedings of The Fourteenth Arctic Marine Oilspill Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 87-106, 1991.
- 33 Fingas, M.F., D.A. Kyle and E. Tennyson, "Physical and Chemical Studies on Dispersants: The Effect of Dispersant Amount and Energy", in *Proceedings of the Sixteenth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 861-876, 1993.
- 34 Fingas, M.F., D.A. Kyle, and E.J. Tennyson, "Physical and Chemical Studies on Oil Spill Dispersants: Effectiveness Variation With Energy", in *Proceedings of The Fifteenth Arctic Marine Oilspill Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 135-142, 1992.

- 35 Fingas, M.F., M. Di Fruscio, B. White and N.D. Stone, "Studies On The Mechanism of Dispersant Action: Weathering and Selection of Alkanes", in *Proceedings of The Twelfth Arctic and Marine Oilspill Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 61-89, 1989.

APPENDIX

DETAILED TEST METHODS

SWIRLING FLASK TEST

Equipment and Supplies:

Platform shaker - (eg. New Brunswick Environmental Shaker Model G27) with a platform fitted with clamps to accept 125 mL Erlenmeyer Flasks.

UV/VIS Spectrophotometer. (The present instrument in use at the Emergencies Sciences Division is a Varian Cary 1 with a 6 cell multi-cell changer using 12 matched semi-micro cells.)

Spectro-Grade Dichloromethane (Methylene Chloride).

Bottom-Spouted Erlenmeyer Flasks (hereafter referred to as swirling flasks) as per figure. These can be purchased by special order from Johns Scientific in Toronto, Canada.

6-25 mL graduated cylinders.

6-125 mL standard separatory funnels with stoppers.

6-25 mL graduated mixing cylinders with stoppers.

5 mL glass pipette.

safety bulb (for glass pipette).

Positive displacement pipettors (variable or fixed) for volumes of 100 μ L, 10 μ L and 5 μ L.

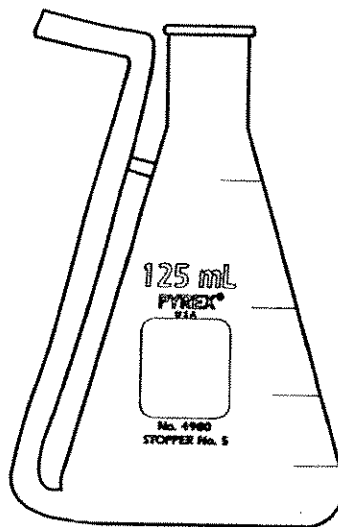
2 timers (preferably countdown timers).

4 L bottle fitted with 100 mL dispensette (calibrated to deliver 60 mL of saltwater accurately. See calibration instructions which follow).

Large container to hold saltwater (66L). Saltwater prepared as per instructions in preparation procedure section.

Salt (rough table salt is sufficient).

Kimwipes



Calibration and Maintenance of Instruments:

In the swirling flask test it is important to ensure that all equipment is running properly and at specified parameters. These include the UV/VIS spectrophotometer, the shakers and the dispensette. The calibration and maintenance procedures for these instruments are as follows:

Shaker:

It is important to ensure that the shaker is rotating at 150 RPM to keep the applied energy constant for each trial. This is accomplished by removing the shaking platform and using a handheld tachometer (eg: Shimpo DT-105) to test the rotation speed of the instrument. The speed on the control panel of the shaker is then adjusted to correspond with a reading of 150 RPM on the tachometer.

The interior of the shaker is cleaned weekly to remove all salt deposits that may have accumulated.

UV/VIS Spectrophotometer:

Due to the nature of the experiment it is essential that the spectrophotometer be checked for accuracy daily and with a more thorough calibration monthly. The daily routine test is performed using a holmium oxide filter. This filter is run after the instrument "warmup" period of one hour. The results of this are recorded and monitored daily.

The monthly tests include a commercially-available spectrophotometer checking kit called Spectro-Chek (marketed by Oxford Scientific) and in some cases an internal test from the instrument software. The Spectro-Chek kit consists of four solutions which enable the user to monitor wavelength reproducibility and linearity of the photocell in both the visible and ultraviolet regions. The internal check verifies the wavelength accuracy, wavelength reproducibility, photometric noise and baseline flatness of the instrument.

Dispensette and 4 L Bottle:

The dispensette is a means to deliver accurate volumes of a solution. In the swirling flask test this solution is salt water. The tendency of saltwater to produce salt deposits causes problems in the accurate delivery. Thus the calibration process is done each time the 4 L bottle is replenished with saltwater. This process consists of measuring the delivered quantity ($2 \times 60 \text{ mL} = 120 \text{ mL}$) in a 250 mL graduated cylinder. The volume can then be adjusted to deliver the required 120 mL of saltwater accurately. The dispensette itself should be washed with clean water to eliminate salt deposits on the exterior since they may inhibit the free movement of the plunger.

Preparation Procedures:

In this test there are three preparation procedures including the premixed sample preparation, saltwater preparation and the calibration curve preparation.

Premixed Sample Preparation:

The premixed sample consists of a known ratio of oil to dispersant. In previous tests, it has been found that the optimal ratio is 25:1 oil:dispersant. This ratio has been studied and found to be the point where a minimum amount of dispersant will yield the maximum dispersion of oils. The actual preparation is done by weight on a precision balance. Samples of approximately 3-4 grams are made for each oil/dispersant combination. These samples are kept in amber vials and stored in a cold room at 15°C when not in use.

Saltwater Preparation:

The saltwater used in this experiment is produced in the laboratory in batches of 66 L. To accomplish this, 2.178 kg of fine granulated salt is added to a large container with a 66 L mark. The container is then filled to this 66 L mark with water and thoroughly mixed.

The residue (from the salt) which floats on the surface is taken off using a large piece of filter paper. This procedure yields a 33 ppt salt mixture which simulates the salt content of the ocean.

Calibration Curve Production Procedure:

The results of this test rely heavily on the accuracy of the calibration curves. Therefore, the production of these calibration curves should mimic the actual test procedure as closely as possible. This implies that all aspects of the extraction process should be followed exactly in producing the calibration curve. The following is a step by step approach to the calibration curve process:

1) Fill a 125 mL separatory funnel with 30 mL (measured in a 50 mL graduated cylinder) prepared saltwater.

2) To each funnel add the appropriate volume of crude oil to yield the % efficiency desired. The volumes used are as follows: 25 μ L=100%, 20 μ L=80%, 16 μ L=64%, 12.5 μ L=50%, 10 μ L=40%, 8 μ L=32%, 6 μ L=24%, 4 μ L=16%, 3 μ L=12%, 2 μ L=8%, 1 μ L=4% and 0.5 μ L=2%.

3) The oil is then extracted as for the swirling flask procedure. The volume of organic extract is 13 mL.

4) The organic extracts are then measured with the UV/VIS spectrophotometer at 340, 370 and 400 nm. The data is then graphed. The particular technique used at ESD is a computerized program, Cricket Graph. The absorbance is plotted on the x-axis and the % efficiency on the y-axis. The equation type is a 2nd degree polynomial using three decimal place accuracy. An example of a calibration curve is shown in the figure below.

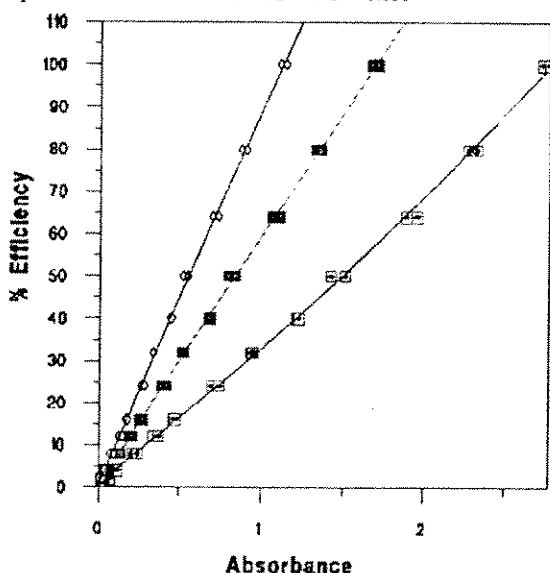
5) All calibration curves are kept on file and updated each time an oil is tested. This is done because oils will slowly weather and thus yield higher absorbance readings.

Sample Oil Calibration Curve for Swirling Flask Test.

$$y = 1.591 + 28.067x + 2.355x^2 \quad r^2 = 0.999 \quad \square \text{ 340}$$

$$y = 0.785 + 55.822x + 0.234x^2 \quad r^2 = 0.999 \quad \blacksquare \text{ 370}$$

$$y = 0.094 + 59.588x + 1.547x^2 \quad r^2 = 0.999 \quad \circ \text{ 400}$$



Test Procedure:

- 1) Using a dispensette, add 120 mL (2 X 60 mL) to each of six swirling flasks. These flasks are then inserted into clamps on the shaking platform and allowed to equilibrate at 20°C for 20 minutes.
- 2) With the flask still in its respective clamp, carefully float the desired sample on the top of the saltwater. There are three separate application procedures which can be followed at this point. These are the a) premixed b) one-drop and c) two-drop methods.

a) In the premixed method a 100 μ L premixed oil/dispersant sample is floated

in the centre of the flask.

b) In the one-drop method a 100 μL oil sample is first floated in the centre of the flask, followed by a 10 μL drop of dispersant. This dispersant drop is applied in the centre of the oil slick.

c) The two-drop method follows the same pattern as the one-drop method except that the dispersant is added as two 5 μL drops. The first drop is added one-third of the way across the diameter of the flask. This will often cause the oil slick to herd to the opposite side of the flask. The second drop is then added two-thirds of the way across the diameter of the flask.

3) The flasks are then swirled in the shaker at 150 RPM for 20 minutes.

4) After the 20 minute shaking time has elapsed, each flask is immediately (and carefully) removed from its clamp and placed on a rack inside the shaker chamber. They are then allowed to settle for 10 minutes.

5) A 30 mL aliquot of the resulting oil in water dispersion is then transferred to a 50 mL graduated cylinder. The swirling flask is tipped so the saltwater and dispersed oil flow freely from the spout. The first 2-3 mL are discarded and then the 30 mL aliquot is transferred to the graduated cylinder.

6) The 30 mL aliquot is transferred to a 125 mL separatory funnel.

7) 5 mL of Dichloromethane is added to each funnel. They are stoppered and shaken vigorously for 15 seconds, degassed into a fume hood and allowed to settle for 2 minutes.

8) 3 mL of the organic (bottom) layer is accurately delivered to a 25 mL graduated mixing cylinder and stoppered.

9) Steps 7 and 8 are repeated twice more with the exception that 5 mL of the organic layer is transferred to the cylinder instead of 3 mL. This will yield a total organic extract of 13 mL. Two mL of organic layer are left in the separatory funnel to avoid contamination of the organic extract with water.

10) The organic extracts are then inserted into the UV/VIS spectrophotometer cells and their absorbances read at 340, 370 and 400 nm.

11) The % efficiency of each sample is calculated for each wavelength by substituting the absorbance readings into the appropriate equation for that oil. The values are averaged to yield the overall % effectiveness for the sample.